

USPTO Customer No. 25280

Case 5601

REMARKS*Rejection under 35 USC 112, first paragraph*

In the Final Office Action mailed May 9, 2005, Claims 1 – 3 and 5 – 22 were rejected under 35 USC 112, first paragraph, because the specification, while being enabling for select embodiments of a polymer having a cohesion parameter of between 13 and 19 MPa^{1/2}, did not reasonably provide enablement for the breadth of polymers that may possess this characteristic.

Claims 1-9 and 21 have been cancelled without prejudice, with Applicant reserving his right to file such claims in a subsequent divisional application. Accordingly, the rejection of these claims has now been rendered moot.

In the response submitted July 11, 2005, to the Final Office Action, Applicant amended the specification to clarify Paragraph 11 and to address the Examiner's concern that certain polymer combinations described in previous patents did not perform as well as those described in the present application.

Applicant draws the attention of the Examiner to such amendment for the purpose of reiterating that the efforts in the previous patents were directed to the formation of interpenetrating polymer networks (IPNs) without an understanding of the thermodynamic principles that enabled one to predict the likelihood of forming an IPN from two given polymers. Applicant has identified a means whereby to predict, with reasonable certainty, the extent of IPN formation, and this means includes selecting polymers with cohesion parameters that are relatively close to one another (e.g., with 3 MPa^{1/2}).

As mentioned previously, Applicant has found that the best indicator of whether a given polymer will dissolve in silicone is the proximity of its cohesion parameter to that of silicone (preferably,

USPTO Customer No. 25280

Case 5601

as claimed, a cohesion parameter within about $3 \text{ MPa}^{1/2}$ of that of silicone). Furthermore, cohesion parameters for a genus of a given polymer are generally identified over a fairly narrow range, making them a reasonable predictor of success in combining with silicone.

Looking at the scope of the claims with respect to the scope of the disclosure, Applicant has provided a list of polymers having a cohesion parameter that is of reasonable proximity (that is, within about $3 \text{ MPa}^{1/2}$) to that of silicone (typically, about $16 \text{ MPa}^{1/2}$). The cohesion parameter proximity is what is claimed in Applicant's Claim 10. Since cohesion parameters for a given genus of polymers are predictably within a fairly small range, the polymers found on pages 10-12 of the specification and in Claim 18 were listed with a reasonable degree of certainty that each would dissolve well with silicone and form an IPN suitable for use as an airbag coating. Thus, Applicant believes the scope of the claims to be commensurate with the scope of the disclosure.

Furthermore, in describing the present invention, Applicant chose polymer cohesion parameters to describe the components, not only because of the high degree of predictability of forming an IPN when a polymer having a cohesion parameter similar to that of silicone is chosen, but also because of the availability of cohesion parameter data for a broad range of polymers.

Unlike polymer characteristics such as molecular weight distribution, structure, or even product name, the cohesion parameter for a given polymer genus and for many specific polymer species is readily available in any public library setting or on the Internet. For example, Applicant identified, on page 10 of the specification, a textbook that is the definitive source of data on polymer solubility parameters (i.e., *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*).

USPTO Customer No. 25280

Case 5601

Included with this response are pages from Chapter 14 of the *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*. Table 1 (p. 280) is representative of the data contained in this chapter and described in our specification. Subsequent tables (not included) list specific examples of Acrylics, Alkyd Resins, Amine Resins, Cellulose Derivatives, Epoxy Resins, Rubber, Hydrocarbon Resins, Phenolic Resins, Polyesters, Polyamides, Rosin Derivatives, Styrene Polymers and Copolymers, Vinyl Resins, and Miscellaneous compounds. This information will be submitted on request.

Further included with this response is a passage beginning on page 308, which describes how a cohesion parameter could be calculated if one had knowledge of the compound structure.

Accordingly, Applicant believes he has satisfied the requirement that "one skilled in the art be able to practice the claimed invention, given the level of knowledge and skill in the art."

* * *

The Examiner has indicated that Claims 6 – 20 would be allowable if rewritten or amended to overcome the rejection(s) under 35 USC 112, first paragraph, as set forth in the Office Action.

Applicant previously cancelled Claims 6 – 9.

Applicant has provided arguments in support of Claims 10 – 20 and 22 to overcome the rejection under 35 USC 112, first paragraph, and to clarify the intended scope of the pending Claims. Applicant believes the application now stands in condition for allowance.

USPTO Customer No. 25280

Case 5601

CONCLUSION

For the reasons set forth above, it is respectfully submitted that the rejections have been traversed and that a formal Notice of Allowability should be issued for the remaining claims.

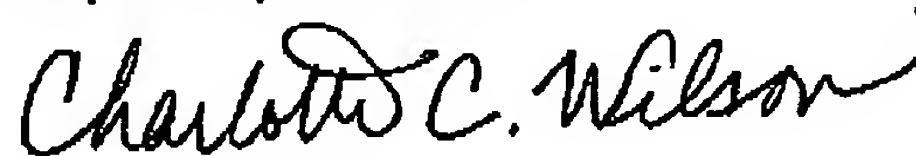
Should any issues remain after consideration of this Amendment and accompanying Remarks, the Examiner is invited and encouraged to telephone the undersigned in the hope that any such issue may be promptly and satisfactorily resolved.

The response is accompanied by a Petition for Extension of Time (three months). In the event that there are fees associated with the submission of these papers (including extension of time fees), authorization is hereby provided to withdraw such fees from Deposit Account No. 04-0500.

Date: October 20, 2005

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CRC Handbook of Solubility Parameters and Other Cohesion Parameters

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Chapter 14

POLYMER COHESION PARAMETERS

If account is taken of the major deviations from regular behavior due to the substantial size difference between polymer and solvent molecules, as described in Section 13.5, cohesion parameters may be applied to polymer solutions just as they are to mixtures of liquids. Because polymers are more often encountered as crystalline or amorphous solid-like materials than as liquids, and because polymers can act as "solvents" as well as "solutes", the use of the more general term "cohesion parameter" is particularly appropriate in place of the rather restrictive title "solubility parameter".

The cohesive pressures of polymers can be evaluated directly by thermodynamic means only for vaporizable materials, although some of the indirect thermodynamic methods of Chapter 7 can be applied in correlations and estimations.^{164,176,328} Also, the concept is directly applicable only to amorphous polymers, and when considering crystalline polymers it is in principle necessary to calculate the activity of the crystalline solid relative to the real or hypothetical amorphous material at the same temperature, as described in Chapter 12. In practice the distinction between amorphous and crystalline polymers is not so clear-cut (Section 16.4), and nonthermodynamic empirical methods are frequently used in the estimation of cohesion parameters for polymers.

In one of the original applications of cohesion parameters to polymer solutions²²⁹ the Hildebrand parameter was combined with a classification into strong, moderate, or poor hydrogen bonding capability, as described in Sections 8.1 and 8.2, and ranges of values for representative polymers are given in Table 1 in order of increasing Hildebrand parameter. A more complete list appears in Table 2, classified by polymer type.

It is incorrect to assume that the "best" solvent for a polymer is necessarily the corresponding monomer or an oligomer (low molecular weight polymer, often liquid) made up of the same repeating units; these liquids usually have cohesion parameters lower than those of the polymers, for reasons explained in Section 14.5. Rather, the best solvent is *another* liquid, with a cohesive energy rather higher than that of the monomer but with a cohesive pressure the same as that of the polymer.

There is a great variety of indirect methods for estimating polymer cohesion parameters, because they are related to so many physical properties, and once determined the cohesion parameters may be used to correlate or estimate values of other physical properties. This chapter deals with some of the relationships between the cohesion parameters and other properties of polymers, but consideration of all chromatographic properties is deferred to Chapter 18. The properties of oligomers are considered in Section 14.6, and copolymers in Section 16.8. Polymer cohesion and adhesion have much in common,⁷⁸⁴ and adhesion is described in cohesion parameter terms in Section 17.5.

An interesting new development which is not discussed in detail here is the discussion of anisotropic or liquid crystal polymer solutions in terms of cohesion parameters.^{434,435,1130,1523} Another area not explored is the control that can be exerted on the rates of polymerization by varying the solvent cohesion parameter.^{731,1367-1373,1379,1380} For example, some polymerizations and copolymerizations are faster in poor solvents than in good solvents, and the cohesion parameters of initiators may be important if there is preferential solvation. Also, from a practical point of view, it can be noted that hydrogenation has the effect of decreasing the Hildebrand parameter of a polymer.¹⁷¹²

14.1 COHESION PARAMETERS FROM POLYMER-LIQUID INTERACTION PARAMETERS

Hildebrand parameters for polymers may be evaluated from polymer-liquid χ parameters

Table 1
 APPROXIMATE HILDEBRAND PARAMETER (δ)
 RANGES FOR SOME COMMON POLYMERIC
 MATERIALS, CLASSIFIED BY HYDROGEN BONDING
 CAPABILITY AND IN ORDER OF INCREASING δ
 VALUES^{1362,1363}

Polymer	Hildebrand parameter ranges (δ /MPa ^{1/2}) in solvents with hydrogen bonding capability which is		
	Poor	Moderate	Strong
Polytetrafluorocarbons	12—13	—	—
Ester gum	14—22	15—22	19—22
Alkyd 45% soy oil	14—22	15—22	19—24
Silicone DC-1107	14—19	19—22	19—24
Poly(vinyl ethyl ether)	14—23	15—22	19—29
Poly(butyl acrylate)	14—26	15—24	—
Poly(butyl methacrylate)	15—23	15—20	19—23
Silicone DC-23	15—17	15—16	19—21
Polyisobutylene	15—16	—	—
Polyethylene	16—17	—	—
Gilsonite®	16—19	16—17	—
Poly(vinyl butyl ether)	16—22	15—21	19—23
Natural rubber	17	—	—
Hypalon® 20 [chlorosulfonated PE]	17—20	17—18	—
Ethyl cellulose N-22	16—23	15—22	19—30
Chlorinated rubber	17—22	16—22	—
Damar gum	17—22	16—21	19—22
Versamid® 100 [polyamide]	17—22	17—18	19—23
Polystyrene	17—22	19	—
Poly(vinyl acetate)	17—19	—	—
Poly(vinyl chloride)	17—23	16—22	—
Phenolic resins	17—24	16—27	19—28
Buna N (butadiene-acrylonitrile copolymer)	18—19	—	—
Poly(methyl methacrylate)	18—26	17—27	—
Carbowax® 4000 [poly(ethylene oxide)]	18—26	17—30	19—30
Thiokol® [poly(ethylene sulfide)]	18—21	—	—
Polycarbonate	19—22	19—21	—
Pliolite® P-1230	19—22	—	—
Mylar® [poly(ethylene terephthalate)]	19—22	19—20	—
Vinyl chloride-acetate copolymer	19—23	16—27	—
Polyurethane	20—21	—	—
Styrene-acrylonitrile copolymer	22—23	19—20	—
Vinsol® [rosin derivative]	22—24	16—27	19—26
Epon® 1001 [epoxy]	22—24	17—27	—
Shellac	—	21—23	19—29
Polymethacrylonitrile	—	22—23	—
Cellulose acetate	23—26	21—30	—
Cellulose nitrate	23—26	16—30	26—30
Polyacrylonitrile	—	25—29	—
Poly(vinyl alcohol)	—	—	25—27
Nylon 6,6 [poly(hexamethylene adipamide)]	—	—	28—31
Cellulose	—	—	30—33

308 *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*

poly[*trans*-bis(tri-*n*-butylphosphine)platinum 1,4-butadiynediyl], retains a rod-like shape in solution, as it exhibits an intrinsic viscosity independent of solvent Hildebrand parameter in the range 13.5–20 MPa^{1/2}, and a uniformly high solubility in these solvents.¹⁵²³ This type of polymer is receiving increasing attention because of special properties in both solid state and solution, including the formation of anisotropic (liquid crystal) polymer solutions.

14.5 CALCULATION OF POLYMER COHESION PARAMETERS

The group contribution methods described in Chapter 6 are generally applicable to oligomers and polymers as well as to low molecular weight liquids. The molar mass of the repeating unit, uM , can be used in place of the monomer molar mass as illustrated below.

The molar enthalpy of vaporization of an oligomer or polymer made up of n repeating units may be subdivided according to

$$\Delta_1^g H = 2 \epsilon \Delta H + (n - 2) ^u \Delta H \quad (36)$$

where $\epsilon \Delta H$ and $^u \Delta H$ are the contributions of the end groups and repeating units, respectively, to the molar enthalpy of vaporization $\Delta_1^g H$. The corresponding molar mass is

$$M = 2 \epsilon M + (n - 2) ^u M \quad (37)$$

where ϵM is the molar mass of the end group and $^u M$ that of the repeating unit. Equation 36 can be rewritten:

$$\Delta_1^g H/M = 2 \epsilon \Delta H/M + \frac{(n - 2) ^u \Delta H}{2 \epsilon M + (n - 2) ^u M} \quad (37a)$$

In polymers, where M is large, $2 \epsilon \Delta H/M$ and $2 \epsilon M$ are negligible, so

$$\Delta_1^g H/M = ^u \Delta H/^u M$$

If the density, $\rho = M/V$, is inserted,

$$\Delta_1^g H/V = \rho ^u \Delta H/^u M \quad (38)$$

and from the definition of the Hildebrand parameter (Equation 6, Chapter 2)

$$\delta = [(\Delta_1^g H - RT)/V]^{1/2}$$

With RT/V negligible because V is large,

$$\delta = (\rho ^u \Delta H/^u M)^{1/2} \quad (39)$$

If this concept is extended^{1665,1668} in terms of group molar attraction constants (Equation 26, Chapter 6),

$$\delta = \sum_i F_i/V$$

then the Hildebrand parameter of an oligomer is

$$\delta = [^u F(V - \epsilon V)/^u V + \epsilon F]/V \quad (40)$$

309

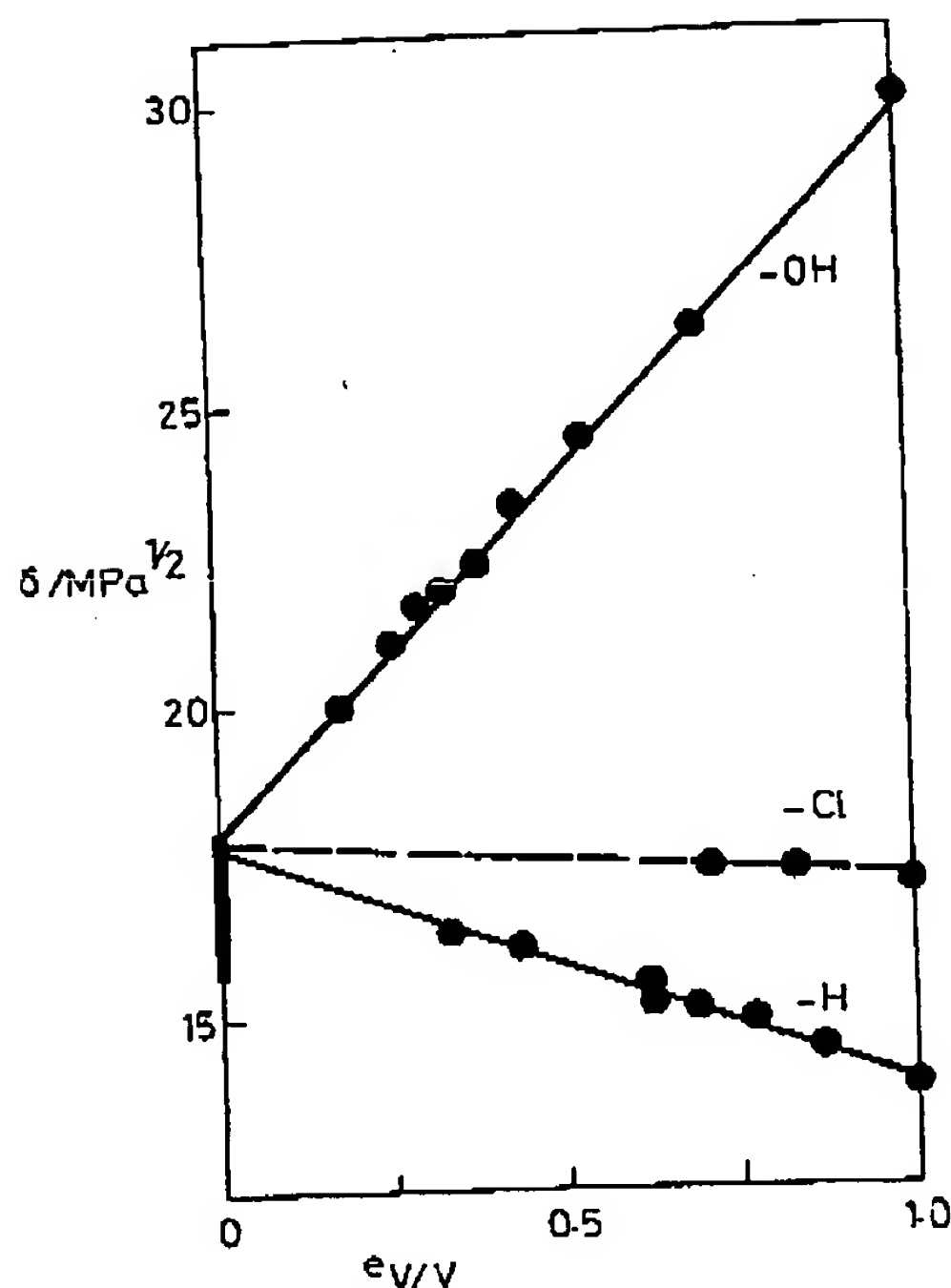


FIGURE 6. Variation of the Hildebrand parameter (δ), at 25°C, of unbranched alkanes (lowest line) and their 1-hydroxy- (upper line) and 1-chloro- derivatives with the ratio of the functional end group volume to the total volume (eV/V) (Equation 41). The bar on the ordinate indicates the range of polyethylene Hildebrand parameter values by other methods. (Adapted from Wolf, B. A., *Makromol. Chem.*, 178, 1869, 1977.)

where the relative number of repeat units is given by $(V - eV)/V$. Using $^uF/V = ^u\delta$ and $^eF/V = ^e\delta$,

$$\delta = ^u\delta(1 - eV/V) + ^e\delta eV/V \quad (41)$$

as indicated in Section 6.6, and for $eV \ll V$ (high polymers),

$$\delta = ^u\delta = ^uF/V \quad (42)$$

From Equation 41 it can be seen that it is possible to evaluate $^u\delta$ from directly observable δ and V values of liquid and volatile monomers and oligomers, using the molar volume of the smallest member of the homologous series as eV . Wolf⁶⁶⁵ has performed this extrapolation for unbranched alkanes and their 1-chloro and 1-hydroxy derivatives (Figure 6). Even for the homologous alcohols (for which the geometric mean rule is not expected to be applicable) the data (including those for water, not shown in the figure) fall on satisfactory straight lines and give $^u\delta$ values within the limits of those obtained by other methods. In another case, cohesive pressures have been obtained from the vapor pressures of oligomers of poly(tetramethylene oxide) and related compounds, resulting in a Hildebrand parameter for the liquid polymer of 17.0 MPa^{1/2}.⁶⁷⁰

310 CRC Handbook of Solubility Parameters and Other Cohesion Parameters

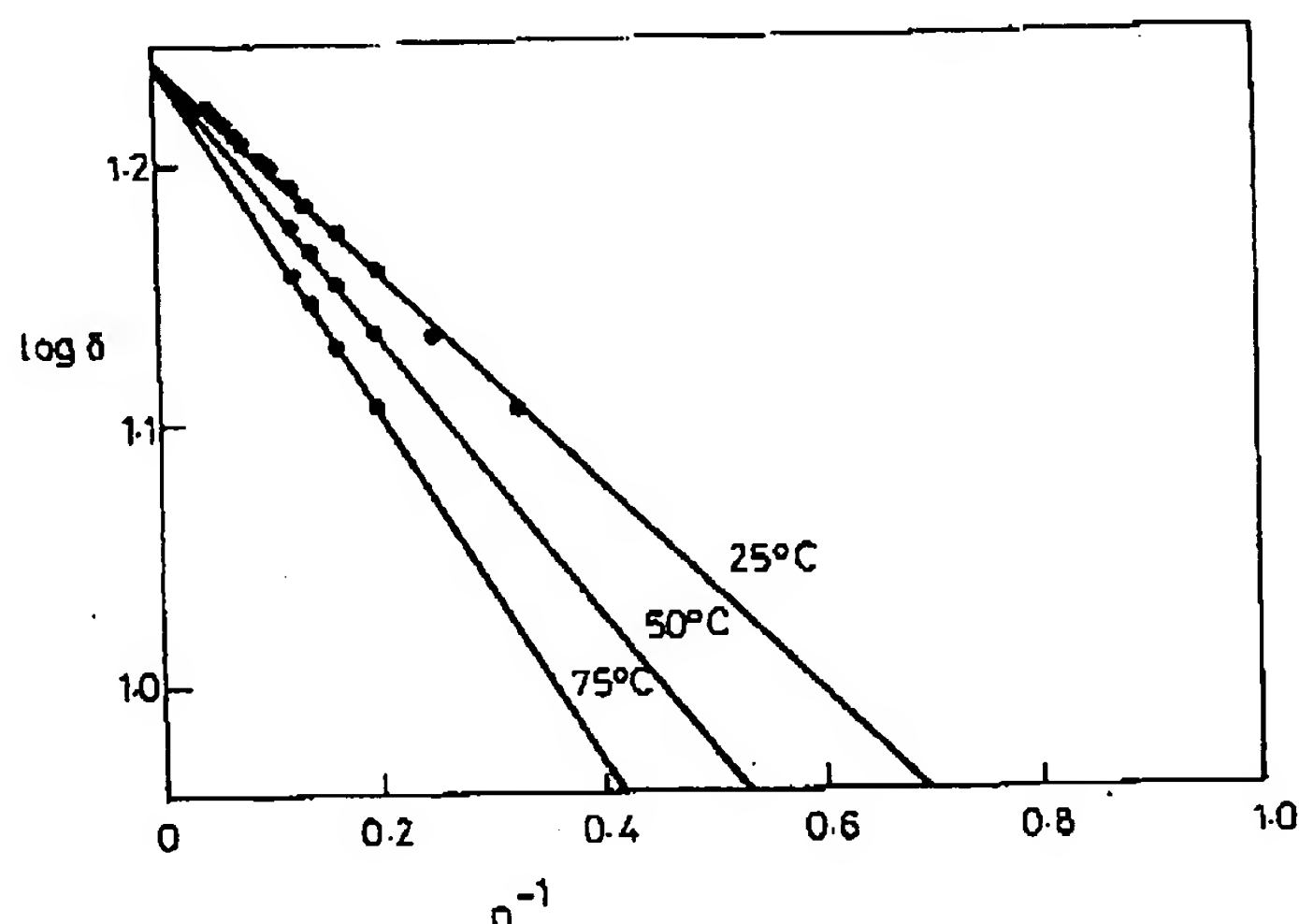


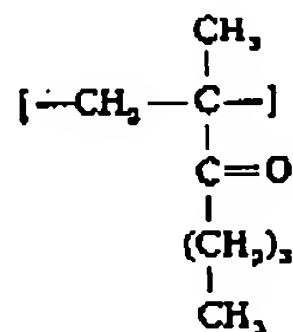
FIGURE 7. The logarithm of the Hildebrand parameter (δ) plotted as a function of the number of carbon atoms (n) at three temperatures. (Adapted from Ritzsch, M. and Krahn, G., *J. Polym. Sci. Polym. Symp.*, 42, 1001, 1973.)

It is also possible to extrapolate Hildebrand parameter values of homologous series to high molar mass by means of relationships such as

$$\log \delta = \log \delta_{\infty} + Bn^{-1} \quad (43)$$

where the coefficient B depends on temperature but δ_{∞} is independent of temperature¹²¹⁶ (Figure 7).

As pointed out in Section 13.1 for polymer group molar volumes, the group contributions to cohesive energies of polymers are not necessarily identical to those for low molar mass compounds. Hoftyzer and van Krevelen¹⁵⁷⁸ have compiled a set of ($-^2U$) values from data on polymers (Table 10). Also, on the basis of the molar attraction constants of Table 8, Chapter 6, for atoms and structural features they derived group molar attraction constants and presented them in the form shown in Table 11 (along with those of Small¹⁴³³ and Hoy⁶⁸¹ for comparison). Examples have also been published^{1667,1578} of the application of the group molar attraction method using these data, for example for poly(butyl methacrylate) (Table 12):



The calculated δ values by both methods are within the range of those reported experimentally (Table 2).

Voeks,¹⁶⁰⁴ and more recently Ahmad and Yaseen,^{15,16,19-21,23-25} have compared the polymer Hildebrand parameters calculated from various sets of group constants. Table 13 gives for

Table 10
MOLAR GROUP
CONTRIBUTIONS TO
POLYMER COHESIVE
ENERGIES AT 25°C

Group, z	$-U/kJ\ mol^{-1}$
$-CH_3$	9.64
$-CH_2-$	4.19
$-CH-$	0.42
$-C-$	-5.58
$-CH(CH_3)-$	(10.06)
$-C(CH_3)_2-$	(13.70)
$-CH=CH-$	10.20
$>C=CH-$	4.86
$-C(CH_3)=CH-$	(14.50)
Phenyl	31.00
p-Phenylene	25.14
-F	4.47
-Cl	12.99
-Br	15.50
-CN	25.00
-CHCN	25.42
-O-	6.29
-COO-	13.41
$-C-N-$	60.76
$\begin{array}{c} O \\ \\ -C- \\ \\ H \end{array}$	
-S-	8.80

Adapted from van Krevelen, D. W.
and Hoftyzer, P. J., *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*. Elsevier, Amsterdam, 1976.

a few polymers an indication of the variation in calculated values, and a comparison with experimental results. Askadskii's van der Waals' method⁷⁴⁻⁷⁷ (Section 6.6) is seen from this table to provide cohesion parameter estimates for polymers in good agreement with those of other methods.

Alternative methods of estimating polymer cohesion parameters are based on theoretical or empirical relationships with other molecular properties. For example, Sewell¹³⁵⁷ used molar refraction, R , by showing for a range of polymers that

$$R/cm^3 = 0.068 (-UV)^{1/2}/J^{1/2} cm^{3/2}$$

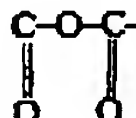
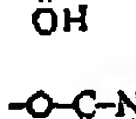
so from Equation 3, Chapter 3, in terms of the refractive index n ,

$$R = \left(\frac{n^2 - 1}{n^2 + 2} \right) V$$

$$\delta/MPa^{1/2} = 14.8 (n^2 - 1)/(n^2 + 2) \quad (44)$$

312 CRC Handbook of Solubility Parameters and Other Cohesion Parameters

Table 11
GROUP MOLAR ATTRACTION
CONSTANTS AT 25°C OF VAN KREVELEN
ET AL.

Group, z	$\delta^2/FJ^{1/2} \text{ cm}^3\text{mol}^{-1}$		
	van Krevelen	Hoy ⁶⁸¹	Small ¹⁴³⁰
-CH ₃	420	303	438
-CH ₂	280	269	272
-CH-	140	176	57
-C-	0	66	-190
-CH(CH ₃)-	560	479	495
-C(CH ₃) ₂ -	840	672	686
-CH=CH-	444	497	454
>C=CH-	304	422	266
-C(CH ₃)=CH-	724	(725)	(704)
Cyclopentyl	1384	1295	—
Cyclohexyl	1664	1473	—
Phenyl	1517	1398	1504
p-Phenylene	1377	1442	1346
-F	164	85	(250)
-Cl	471	420	552
-Br	614	528	696
-CN	982	723	839
-CHCN-	1122	(902)	(896)
-OH	754	462	—
-O-	256	235	143
-CO-	685	538	563
-COOH	652	(1000)	—
-COO-	512	668	634
-O-C(=O)-O-	767	(904)	—
	767	1161	—
-C(=O)-N-	1228	(906)	—
	1483	(1037)	—
-S-	460	428	460

Adapted from van Krevelen, D. W. and Hoftyzer, P. J., *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*, Elsevier, Amsterdam, 1976.

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